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Origin of the Partially Localized State in a 2D Molecular Nanoporous Network

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0. Abstract

Two-dimensional organic and metal-organic nanoporous networks can scatter surface electrons, leading to their partial localization. Although such quantum states were initially assigned to intrinsic surface states of the substrate material, this has not been experimentally verified. To this end, we studied the thermally induced energy shifts of the electronic band stemming from coupled quantum states hosted in a metal-organic array formed by a perylene derivative on Cu(111) and compared it with the Cu(111) Shockley state. We observed by angle-resolved photoemission spectroscopy (ARPES), that both, the pristine and the partially localized states, shift by the same amount to higher binding energies upon decreasing the sample temperature, providing evidence for their common origin. Our experimental approach and results validate the use of surface states for modelling these systems, which are expected to provide new insight into the physics concerning partially confined electronic states: scattering processes, potential barrier strengths, excited state lifetimes or the influence of guest molecules.

1. Introduction

Surface states emerge as additional solutions of the Schrödinger equation due to the sudden termination of the 3D periodic bulk. They are located in the projected bulk band gaps and localized at the outermost atomic layers. Surface states provide ideal systems to study low dimensional electronic properties and are extremely sensitive to surface defects such as adsorbates or steps [1-6].

Noble metals exhibit such surface states, generally referred to as Shockley states [7], which generate a quasi-two-dimensional, nearly-free electron gas from *sp*-derived states in the direction parallel to the surface plane, but are confined by the vacuum barrier and the bottom of the projected bulk band gap perpendicular to it [8]. In particular, (111) terminated crystals accommodate their Shockley states at the center of the surface Brillouin zone with well-defined effective mass and parabolic energy dispersion relations [9,10]. The energy onset of these Shockley states is related to the position of the projected bulk band gaps, which are highly sensitive to temperature-induced variations of the lattice constant, causing the supported Shockley state to shift in energy [11].

Previous works have already demonstrated that Shockley electrons can be confined parallel to the surface by artificially built nanoscale assemblies [12-15]. A similar electron localization has been shown in two-dimensional (2D) organic nanoporous networks [4,16-18]. Owing to their periodicity, these networks can be considered as arrays of quantum boxes. However, such confinements are often imperfect, allowing for some degree of coupling between neighboring pores that gives rise to shallow dispersive electronic bands [16]. Based on semiempirical models, the resulting electronic band has been assumed to originate from the pristine surface state [4], but such claim has still to be experimentally demonstrated.

In this letter, we study the temperature dependence of the electronic structure which arises from the interaction of the Cu-coordinated triply dehydrogenated perylene derivative DPDI (4,9-diaminoperylene quinone-3,10-diimine) porous network on Cu(111) using angle-resolved photoemission spectroscopy (ARPES). In dependence of both the sample temperature and the network coverage, we investigate the evolution of the Shockley and the partially localized states. We find that both electronic states experience identical energy shifts upon varying the sample temperature. This provides evidence that the partially localized state indeed originates from the Shockley state and appears modified by the potential of the molecular network.

2. Experimental details

ARPES measurements were performed in UHV (ultrahigh vacuum) conditions (base pressure of 1×10^{-10} mbar) with a lab-based experimental setup equipped with a display-type hemispherical electron analyzer (SPECS Phoibos 150), an energy/angle resolution of 40 meV/0.1° and a monochromatized Helium I ($h\nu=21.2$ eV) source. Variable temperature measurements were

performed using a closed-cycle He cryogenic manipulator with a controlled temperature range between 350 K and 35 K.

The STM (scanning tunneling microscopy) measurements were carried out at both low temperature (Omicron Nanotechnology GmbH with Nanonis SPM control system) and room temperature (home built STM). The bias voltages given in the manuscript refer to a grounded tip. The measurements were performed with Pt-Ir tips (90% Pt, 10% Ir) prepared by mechanical cutting and followed by in situ sputtering with Ar⁺ ions and controlled indentation in the bare Cu(111) substrate. STM data were acquired in constant current mode and were processed with the WSxM software [19].

The Cu(111) surface was cleaned by repeated cycles of Ne⁺ sputtering at energies of 1.0 keV, followed by electron bombardment annealing at 800 K. This resulted in a clean and well-ordered surface as verified by the spectral linewidth of the Cu(111) Shockley surface state [9].

DPDI [20-22] was sublimed from a Knudsen cell ($\sim 240^\circ\text{C}$) onto Cu(111) held at RT in wedge geometry from 0 to 1 monolayer (ML) coverage as shown in **Fig. 1(a)**. 1 ML is defined as saturating the surface with molecules in the closed-packed assembly [22]. Prior to deposition, the molecular rate was monitored by a quartz crystal microbalance. Subsequent to deposition of the well-defined coverage gradient of DPDI, the sample was annealed to 550 K [23] such that a homogeneous Cu-coordinated metal-organic network was generated in the lower coverage regions of the wedge, similar to the model depicted in **Fig. 1(b)**. This nanoporous arrangement led to a sharp and intense signal visible in the ARPES channel plate detector close to the Fermi energy [16].

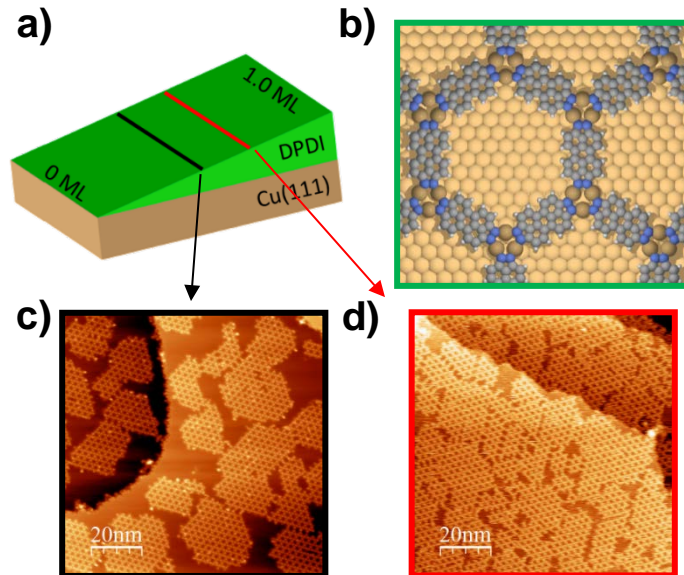


Figure 1. A variable density quantum box array realized through a coverage wedge geometry. (a) Schematic view of the DPDI deposition wedge performed on Cu(111). **(b)** Structural model for the Cu-coordinated 3deh-DPDI nanoporous network forming a p(10x10) superstructure on Cu(111) (adapted from Ref. 22)). **(c, d)** STM images for 0.45 ML (left) (4 K, -0.8 V, 5 pA) and 0.65 ML (right) (297 K, 2 V, 6 pA)

network coverage. The network structure is maintained throughout the wedge up to ~ 0.73 ML. The coverage wedge allowed us to study different network density regions within the same sample preparation (see **Fig. 1(a)**). In essence, well-formed molecular network islands progressively colonize the surface as the molecular coverage is increased, as shown by the STM images of **Figs. 1(c) and (d)** (0.45 ML and 0.65 ML, respectively) [21]. Above the critical coverage of ~ 0.73 ML, the porous network collapses into a close-packed assembly [22].

3. Results and discussion

ARPES spectral functions close to the Fermi level were systematically acquired as function of sample temperature for two coverage regions: the first, where the molecular network completely covered the surface (~ 0.75 ML) and the second, where it coexisted with molecule-free areas (~ 0.50 ML) (close to the coverage of **Fig. 1(c)**). The probed temperature range expands from 315 K to 136 K.

Figure 2(a) shows the ARPES spectral function corresponding to the temperature extremes for ~ 0.50 ML DPDI. The intensity distributions $I(E-E_F, k_{||})$ reflect a coexistence of the Cu Shockley state band originating from the molecule-free areas and the partially localized state band arising from the coupling between pores, in agreement with Ref. 16. While the former has an upward parabolic dispersion [9], the latter exhibits a lower binding energy at $\bar{\Gamma}$ due to partial confinement effects together with an apparent increase of the effective mass [24]. As the temperature of the sample decreases from 315 K to 136 K, both electronic bands become better defined and gain amplitude [9,25]. As expected, the bottom of the Cu Shockley state band shifts towards higher binding energy [11], but it is difficult to discern the behavior of the partially localized state band from the raw data. To follow its evolution, the energy distribution curves (EDC) of the ARPES spectral functions at $\bar{\Gamma}$ ($k_{||} = 0$) are represented in **Fig. 2(b)** for both end temperatures, red being the higher temperature spectrum and blue the lower one. We observed that the well-known Shockley state (SS) band minimum (peak closest to $E_F = -0.40$ meV) was shifted away from the Fermi energy by ~ 30 meV as the sample was cooled down. The same trend was observed on the shoulder feature located in the proximity of $E_F = -0.25$ eV. This peak corresponds to the partially localized state (PLS) and is in part masked by its proximity to the Shockley state. For a better visualization of the thermal energy shift of this state, it is best to study the higher coverage regions which lack the molecule-free areas, and for which the Shockley state is thus quenched. This case is shown in **Fig. 2(c)**, corresponding to 0.75 ML and exhibiting only band attributable to the porous network. Once more a clear energy shift of the band minimum and a sharpening of the features were observed as the temperature was lowered. The comparison between the temperature dependent EDCs, represented in **Fig. 2(d)**, unambiguously shows that the PLS shifts around 30 meV to higher binding energies as the sample is cooled down.

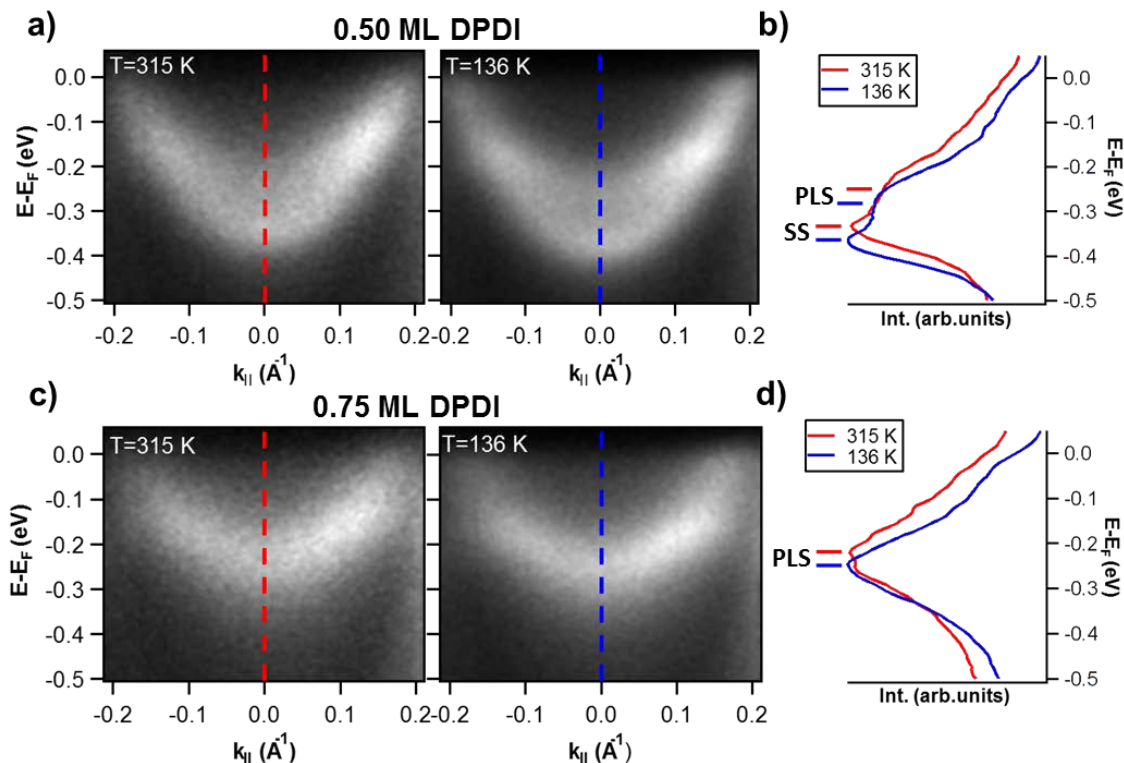


Figure 2. Temperature dependence of the network partially localized state band and Cu Shockley state band at the two extreme temperatures studied. **(a)** ARPES experimental spectral function acquired at 315 K and 136 K for the coverage of 0.50 ML, in which regions of the network and molecule-free areas coexist. **(b)** Smoothed, normal emission ($k_{||}=0$) energy distribution curves (EDCs) for both temperatures in **(a)**. The horizontal lines mark the energy positions of the Cu Shockley state (SS) and the partially localized state (PLS) band minima obtained from a two component Lorentzian fit. **(c)** ARPES experimental spectral function acquired at 315 K and 136 K for the coverage of 0.75 ML featuring the surface completely covered by the network. **(d)** Smoothed, normal emission ($k_{||}=0$) EDCs for both temperatures in **(c)** with horizontal lines indicating the energy positions of the partially localized state band minimum.

The nature of the energy shift observed for the PLS is still undefined at this stage, and we thus followed the temperature transition at intermediate points. The Shockley state of Cu(111) has been shown to linearly shift with temperature, with a slope of $(1.8 \pm 0.1) \times 10^{-4}$ eV/K [11]. For the nanoporous network, EDC waterfall plots at normal emission for the studied temperature range are shown in **Figs. 3(a)** and **(b)** corresponding to full network coverage (0.75 ML) and to coexisting regions of molecular network and molecule-free areas (0.50 ML). We observed that the energy position of the band minimum of the PLS as well as the Cu SS shifted in a linear, progressive way as the temperature was varied. There were no abrupt energy changes of the features, which sharpened up as the temperature was lowered.

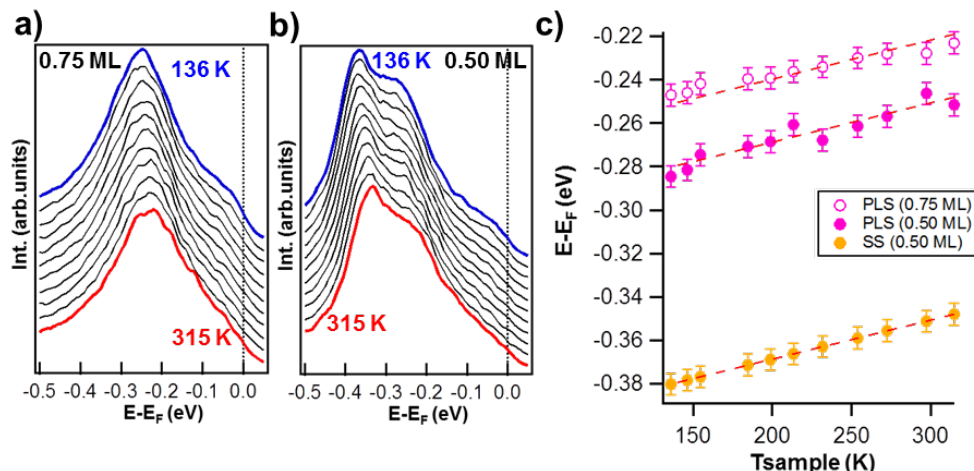


Figure 3. Full range temperature dependence of the partially localized state (PLS) and Cu Shockley state (SS). Normal emission EDC temperature waterfalls for 0.75 ML **(a)** and 0.50 ML **(b)** coverages. A clear trend towards higher binding energy and a sharpening of the features is observed as the temperature is lowered. **(c)** Temperature variation of the energy position of the PLS and Cu SS band minima as extracted from the fit for each spectral line represented in the waterfall. The fit was carried out using one (0.75 ML) or two (0.50 ML) Lorentzian components convoluted with a linear background. The dashed lines correspond to variation rates with a common slope for the three components, all of which agree with the Shockley state variation reported in Ref. 11.

A quantitative analysis of the temperature dependence of these states was achieved by Lorentzian fitting and convolution with a linear background from the spectra in **Figs. 3(a)** and **(b)**. **Fig. 3(c)** summarizes the results from such analysis and shows the variation of the initial state energy with sample temperature. As expected, the Cu SS band (yellow dots) follows the red dashed line which accounts for a rate of $(1.8 \pm 0.1) \times 10^{-4}$ eV/K, in agreement with Paniago et al. [11], resulting in an increase of 32 ± 2 meV in binding energy for the investigated temperature range. The other two sets of magenta points in **Fig. 3(c)** correspond to the PLS for the 0.50 ML (full circles) and 0.75 ML (open circles) and differ in energy by ~ 30 meV. We attribute this offset to a slight excess of molecular coverage [22]. For 0.5 ML the PLS is shifted 33 ± 5 meV within the probed temperature range, which agrees with the variation of the SS, while a slightly smaller shift of 26 ± 5 meV was measured for 0.75 ML. This is still consistent with the SS behavior within the experimental error, and the deviation can be again related to the uncontrolled structural changes arising from excess molecular coverage.

The demonstration that the PLS associated with the nanoporous network exhibits an identical temperature variation of its energy as the surface state of the clean Cu(111) substrate, supports the claim that both have the same Shockley nature. Indeed, no abrupt energy changes are observed and the same temperature dependence is found even when the network fully covers the surface. Hence, upon the network formation, the surface state electrons are subjected to a 2D finite periodic potential imposed by the network structure. The network thus alters the Shockley state giving rise to the scattering phenomena capable of generating new band structures with

different dispersion relations [4,16]. The experimental evidence presented in this study validates the assumption that electrons partially localized within the molecular pores originate from the Shockley state [4,16-20,24]. This rationale should be extensible to other substrates supporting surface states.

4. Conclusion

In conclusion, in this experimental study we shed light onto the origin and nature of the partially localized state observed in a 2D metal-organic nanoporous network self-assembled on the Cu(111) surface. By studying the temperature dependence of two different coverage regimes of the network, we could show that the partially localized state existing in the pores of the network originates from the Cu(111) Shockley state. The energies of both states display the same temperature dependence, directly relating the PLS to the Shockley state observed on the pristine metal surface. This experimental demonstration confirms previous assignments that the surface state electrons are affected by the periodic molecular potential of the network. From this evidence, semi-empirical models can be confidently used to derive the observed electronic states and even to model the surface potential created by molecular networks.

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